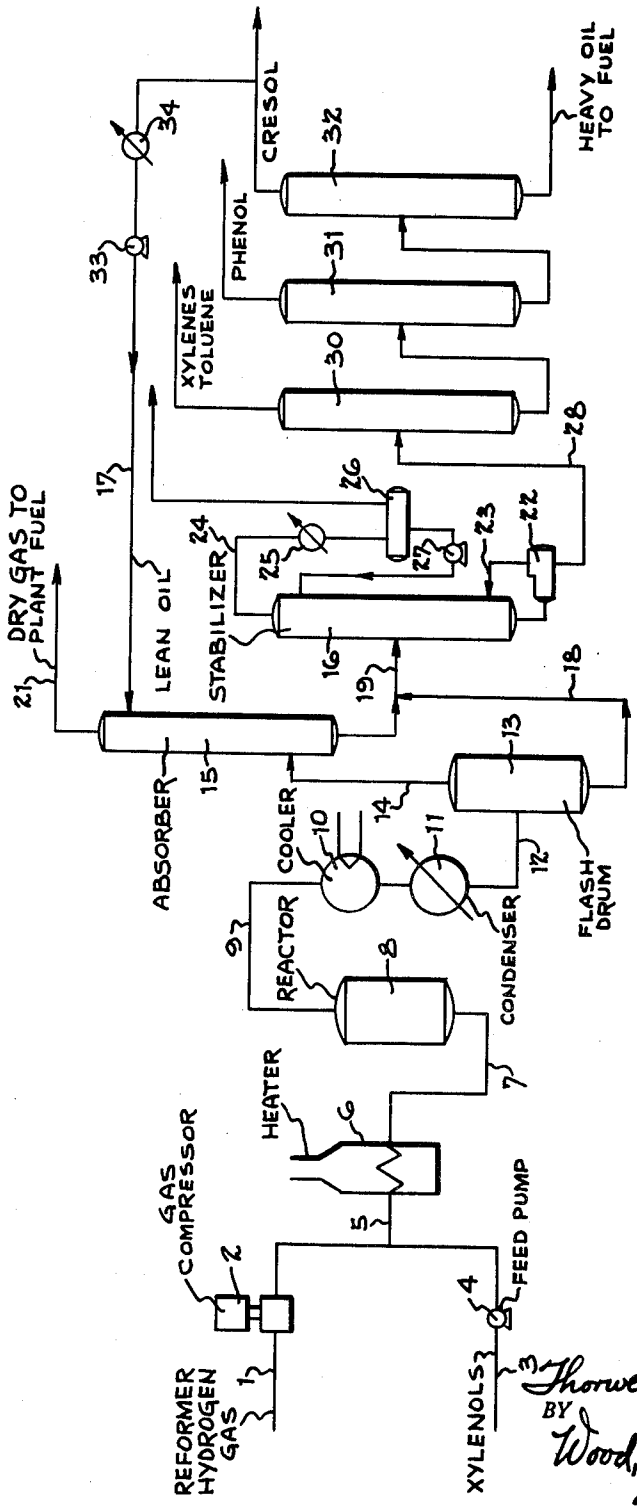
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PRODUCTION OF PHENOLS

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PRODUCTION OF PHENOLS

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This invention relates to the treatment of coal tar by-products for the recovery of phenols therefrom. It is directed particularly to the catalytic removal of methyl and hydroxyl radicals from xylenols which are produced as residual by-products in the distillation of coal tar light oils.

In a copending patent application Serial No. 728,620, filed April 15, 1958, now U.S. Patent No. 2,951,886, issued September 6, 1960, of which this application is a continuation-in-part, a process is disclosed and claimed for recovering benzene of high purity from coal tar light oil by subjecting it to catalytic cracking conditions in the presence of hydrogen at a temperature above approximately 1200° F. By this process toluene and xylene which are present with benzene in coal tar light oil are demethylated into benzene, while paraffins, and thiophenes, and other sulfur compounds which also contaminate the coal tar light oil are destructively removed. By the use of a catalyst comprising 10–15% chromia on a high purity, low sodium content, gamma type alumina support, formation of coke and gas, which would otherwise be expected from the high cracking temperature, is very low. By this means coal tar light oil or crude benzene, which in itself is of limited utility, is readily converted into benzene of high purity for which there is great chemical demand.

An important objective of the present invention is to provide an equally convenient means for converting into useful products mixed xylenols which are produced as residual by-products in the recovery of crude benzol or coal tar light oil from coal tar. As was the case with crude benzol, the xylenols at present are of limited market value. Because of the contaminating constituents of these crude products, relatively pure chemicals cannot be obtained from them at reasonable cost. However, the present invention provides a process for converting crude xylenols into relatively pure chemicals for which a high demand has long continued.

Briefly, the present invention is based upon the discovery that the methyl and hydroxyl groups attached to the benzene rings in the isomers constituting a typical mixed xylenol derived from coal tar can selectively be cracked therefrom, and the sulfur impurities such as thiophenes as well as paraffinic compounds which are present can be removed by subjecting the mixed xylenols to hydrocracking conditions in the presence of a specific catalyst and that the formation of gas and coke from destructive decomposition in such operation may be held to an inconsequentially low figure even at temperatures above 1200°–1250° F.

More specificaly, the present invention is based upon the discovery that the xylenols in a mixed xylenol product derived from coal tar may be converted and thereby up-graded into a product containing phenols in admixture with benzene, toluene, xylene, and cresols, by catalytic hydrodealkylation in a rapid and convenient manner and at relatively low equipment cost. According to the process of the present invention, mixed xylenols are subjected to catalytic cracking in the presence of hydrogen at temperatures of from approximately 1050°–1250° F. or higher in a single pass, with high yield.

While temperatures of the order heretofore have been known to produce destructive effects upon benzenoid hydrocarbons, this adverse effect appears chiefly to have

been caused by the nature of the catalysts previously used. However, I have found that a catalyst consisting of approximately 10–15% by weight of chromia oxide on a high purity, low sodium content, gamma type alumina support is capable, in the presence of hydrogen, of causing selective demethylation and dehydroxylation of mixed xylenols and of promoting concurrent conversion of sulfur-bearing and paraffinic impurities with little or no coking effect. A particular catalyst which enables such results to be obtained is commercially available from the Girdler Corporation, Louisville, Kentucky, under their trade designation G–41. X-ray defraction patterns show the chromia oxide to be present in the form of hexagonal crystals as distinguished from chromia aluminum co-gel catalysts which have also been available but which are incapable of providing similar results. The total chromia content of the commercial product is calculated as 11.8% Cr_2O_3 by weight, the remainder of the product being the specified high purity, low sodium content, gamma type alumina. In use the catalyst is employed in the form of tablets, for example, 3/16" x 3/16" in size, forming a fixed bed through which the feed stock and hydrogen are passed continuously.

The process of this invention is effected by contacting a charge of mixed xylenols with the catalyst and hydrogen at a temperature of the order indicated at a suitable operating pressure, for example, 500 p.s.i.g., and for a short contact time, for example 5 to 100 seconds depending upon the operating condition of temperature and pressure and preferably about 15 to 25 seconds. At temperatures of the order of 1040° F., a substantial proportion of benzene, toluene, and xylene are produced from the mixed xylenols but, in a single pass treatment, a substantial proportion of the mixed xylenols remains unconverted. However, at temperatures of 1235° F. or higher substantially all of the mixed xylenols are usefully demethylated, and phenol constitutes a substantial percentage of the products of conversion in conjunction with benzene, toluene, xylene, and cresols. Thus, for single pass operation, a temperature of approximately 1235°–1250° F. is preferred. Phenol readily may be recovered from the mixed products of conversion by fractional distillation. Therefore, mixed xylenols, for which there heretofore has been a limited market, constitutes a source of a very valuable product.

In the conventional high temperature coking of coal, as has ben practiced in the past, the mixed xylenol content of the coal tar is relatively low in comparison with the crude benzol and cresol content. However, in the more recently developed low temperature process of coal carbonization, mixed xylenols constitute a large part of the coal tar. Thus, mixed xylenols for which there is no substantial demand even in the limited quantities produced in conventional coke oven operation, become such a drug on the market as to affect the economic utilization of the more modern, low temperature coal carbonization process. However, by the process of the present invention mixed xylenols may be converted into phenols and benzene of high purity, for both of which a great demand exists and is likely to increase.

In the practice of the process since demethylation occuring in the charge stock is accompanied by heat liberation, the feed is preferably held at a temperature somewhat lower than the preferred 1235°–1250° F.; for example, the feed temperature may be approximately 1150° F. Control of the feed temperature thereby provides a convenient means of limiting peak temperature at the contact zone.

Within the contact zone demethylation and dehydroxylation occur rapidly but selectively. Even at the high temperature at which cracking is conducted, there is little destructive cracking of the hydrocarbons into coke

or normally gaseous products and little undesirable polymerization. It is to be noted that neither demethylation nor dehydroxylation of the xylenol is complete, as shown by the substantial percentage of phenol and some cresol in the end product, as well as the substantial percentages of toluol and xylene. Sulfur impurities are converted into hydrogen sulfide and paraffinic impurities are cracked to gas.

Following the catalytic treatment, the mixed products of conversion from the hydrocracker are condensed to liquid, and the gaseous products are separated from the liquid products by means of a flash drum and absorber. Dry gas products may be used for plant fuel, while the liquid products are stabilized by removal of entrained or absorbed gas. The liquid products are then subjected to fractionation for the separation of benzene, toluene, and xylene from the phenol and cresol as desired.

One method of practicing the invention continuously on a commercial scale as an adjunct to petroleum refining operations is illustrated in the accompanying diagram, according to which the hydrogen employed for the hydrocracking operation is furnished as hydrogen off-gas from a catalytic reformer. This is supplied through line **1** to a gas compressor **2**. Xylenol-containing feed stock is supplied through line **3** to a feed pump **4**. Hydrogen gas and the charge stock, commingled in line **5**, pass through a heater **6** wherein the temperature is elevated sufficiently to inaugurate or support selective cracking or to provide the desired autocatalytic effect; for example, the feed stock may be preheated to a temperature of 1150° F. or more depending upon the weight/hourly/space velocity in the reactor. It will also be understood that the reactor may be provided with a coolant system for temperature control.

The hot feed stream passes through line **7** to reactor **8** wherein a suitable pressure, for example approximately 500 p.s.i.g., is maintained, as provided by the compressor **2** and feed pump **4**. The reactor contains a fixed bed of catalyst as described, through which the feed material is passed. Flow rate preferably is adjusted to provide a contact time or time of residence within the reactor of approximately 15 to 25 seconds. As will be understood by those skilled in the art, the reactor pressure may be varied from approximately 100 to 1000 p.s.i.g., the 500 p.s.i.g. pressure disclosed herein being an operating pressure which is practical to employ.

A weight/hourly/space velocity of approximately 0.5 to 2.0 pounds of xylenol feed per pound of catalyst per hour is suitable. The molar ratio of hydrogen to hydrocarbon may be from approximately 2:1 to 10:1; a ratio of approximately 5:1 has been found to provide very satisfactory results. These ratios, of course, may be varied to accommodate variations in the composition of the feed stock; for example, mixed xylenols produced in the low temperature carbonization of coal may consist of approximately 97% xylenols and 3% C_9 phenols with little or no cresol, while mixed xylenols from coal tar fractions produced by other processes may contain significant quantities of cresol and varying percentages of paraffinic and substituted phenolic constituents.

The reactor output passes through line **9** and a cooler **10** into a condenser **11** wherein the liquid product is condensed. The output stream then passes through line **12** into a flash drum **13** which may be maintained for example at a pressure of approximately 490 p.s.i.g. and a temperature of 100° F. Gases non-condensible from the flash drum conditions of temperature and pressure are liberated from the stream at this point.

Gases from the flash drum **13** pass through line **14** into an absorber **15** which may be held at a pressure of approximately 450 p.s.i.g. and a temperature of 100° F. The absorber operates in conjunction with a stabilizer **16** and a recirculating cresol product stream may be passed into the absorber as lean oil through line **17**. Liquid product collected in the flash drum, as withdrawn through line **18** therefrom, is commingled with fat oil from the absorber in line **19**. In this manner valuable liquid product contained in the flash drum vapor is recovered in the absorber while the dry gas from the absorber is withdrawn through line **21** for use as plant fuel. The stabilizer may be operated for example at a temperature of approximately 155° F. and a pressure of 75 p.s.i.g. The necessary heat of vaporization for the stabilizer is supplied by reboiler **22** with the vapors returning to the stabilizer through line **23**. Also, the stabilizer overhead, withdrawn through line **24**, operates in conjunction with a reflux system comprising condenser **25** and receiver **26**, the liquid reflux collecting in the receiver at a temperature of approximately 100° F. and being recirculated to the stabilizer by pump **27**.

The stabilizer bottoms are withdrawn through line **28** and may be passed into a fractionation system comprising three or more fractionating columns which may be of conventional design. For example, the fractionating system shown comprises fractionating columns **30**, **31**, and **32**. The first fractionator **30** fractionates out a mixture of benzene, toluene, and xylenols while the bottoms product of this tower is then pumped to the second fractionator, **31**, where the phenol product is separated as overhead. The bottoms product of tower **31** is then pumped to the third fractionator, **32**, which produces cresol overhead while the bottoms product is a heavy oil which may be used for fuel if desired. In the system shown, a portion of the cresol overhead is withdrawn from the output stream by means of pump **33** which feeds to absorber lean oil line **17**. A coolant **34** is installed ahead of the pump **33**, which cools the product to a temperature of approximately 100° F.

The following table illustrates the results obtained in the catalytic conversion of a typical mixed xylenol product under different sets of operating conditions A, B, and C.

Isomer distribution of feed and products—typical runs

	Feed	Run A	Run B	Run C
Weight/hourly/space velocity	-------	1.0	0.8	0.8
Hydrogen-hydrocarbon, mol ratio	-------	4:1	5:1	5:1
Temperature, °F	-------	1040	1150	1235
Liquid recovery, wt. percent (feed =100 wt. percent)	100	89.0	86.0	79.0
Isomer analysis of liquid, wt. percent:				
Benzene, toluene, xylene	-------	24.1	16.1	42.3
Phenol	0.3	2.5	6.9	20.7
Cresols	0.8	10.1	19.4	18.3
Xylenols	95.5	50.9	48.8	6.3
C_9 Phenols	3.4	3.6	1.6	0.3
Water	-------	4.5	3.7	5.6
Residue[1]	-------	4.1	2.7	5.6
Loss	-------	0.2	0.8	0.9
	100.0	100.0	100.0	100.0

[1] Distillation at 50 mm.

The xylenol feed material treated according to the above examples was a commercial stock having 8° API gravity. The operating pressure in each of runs A, B, and C above was 500 p.s.i.g.

It will be noted from this data that the yield of liquid product is high, as is the yield in terms of phenol in run C where the operating temperature was 1235° F. The unusual and unexpected result provided by the present invention is that a catalyst possessing such a high degree of catalyst activity is nevertheless selective in its action and does not destructively degrade the useful components of the feed.

While the invention has been disclosed principally in relation to the recovery of useful products from mixed xylenols, the invention is also useful for other types of charge stocks such as mixed cresols and the like. Moreover, it will be noted that the process of this invention, utilized in conjunction with the process dis-

closed in the aforesaid copending application Serial No. 728,620, enables large quantities of benzene and phenol to be produced of a quality and purity not otherwise obtainable from coal tar fractions. Thus, by conventional distillation of coal tar, whether obtained from the high temperature or low temperature carbonization of coal, to recover light oil and residual mixed xylenols, and by catalytic hydrodealkylation of the respective separated fractions as disclosed in this and the copending application, high quality benzene is obtained from the former and from the latter a mixture which readily may be separated into its phenol, benzene, toluene, and cresol components.

Having described my invention, I claim:

1. A method of treating mixed xylenols derived from coal tar which method comprises, subjecting the mixed xylenols to catalytic hydrocracking conditions in the presence of hydrogen and a catalyst consisting of approximately 10 to 15% by weight of chromia on a high purity low sodium content gamma type alumina support at a temperature in the range from approximately 1040° F. to approximately 1250° F., at a pressure in the range from about 100 to 1000 p.s.i.g., and for a period of time from about 5 to about 100 seconds, to demethylate and dehydroxylate at least some of the xylenols and to destructively crack sulfur and paraffinic impurities therein to gas.

2. The process of claim 1 wherein the hydrocracking temperature is approximately 1235° F.

3. The process of claim 1 wherein the catalytic hydrocracking operation is conducted in the presence of hydrogen off-gas obtained from a catalytic reformer.

4. The process of claim 1 wherein the catalyst consists of approximately 11.8% chromia on said support.

5. The process of claim 1 wherein the chromia is in the form of hexagonal crystals.

6. The process of claim 1 wherein the hydrocracking operation is conducted by passing a stream of said xylenols through a fixed bed of the said catalyst.

7. A process for obtaining phenol from xylenols which process comprises, subjecting the xylenols to catalytic cracking conditions in the presence of hydrogen and a catalyst consisting of approximately 10 to 15% by weight of chromium oxide on a high purity low sodium content gamma type alumina support, at a temperature in the range from approximately 1200° F. to approximately 1250° F., at a pressure in the range from about 100 to 1000 p.s.i.g., for a period of time from about 5 to about 100 seconds, and separating phenol from the liquid product resulting from the treatment.

8. A process for selectively splitting methyl and hydroxyl groups from xylenols in a xylenol-containing feed stock to form simpler products therefrom, said process comprising, contacting said xylenol-containing feed stock in the presence of hydrogen with a catalyst consisting of approximately 10 to 15% by weight of chromia, the balance of the catalyst composition being high purity low sodium content gamma type alumina, at a temperature of from approximately 1040° F. to approximately 1235° F., at a weight hourly space velocity of from about 0.5 to about 2.0, and at a pressure in the range from about 100 to about 1000 p.s.i.g.

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